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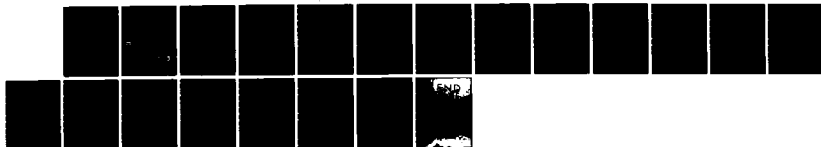
LASER SPECTROSCOPY OF ALKALI ATOM-TETRAHALOETHYLENE  
REACTIONS(U) NEW HAMPSHIRE UNIV DURHAM DEPT OF PHYSICS  
J W WRIGHT AUG 84 AFWL-TR-83-132 F29601-82-K-0068

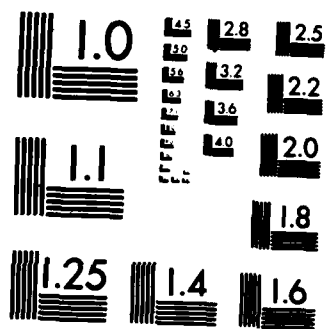
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## LASER SPECTROSCOPY OF ALKALI ATOM-TETRAHALOETHYLENE REACTIONS

John J. Wright

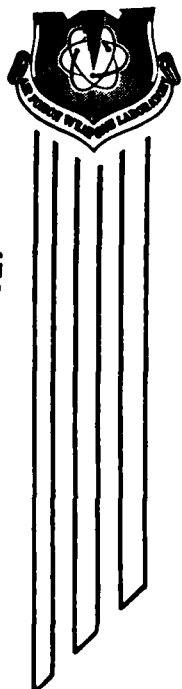
University of New Hampshire  
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August 1984

Final Report

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Air Force Systems Command  
Kirtland Air Force Base, NM 87117

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This final report was prepared by the University of New Hampshire, Durham, New Hampshire, under Contract F29601-82-K-0068, Job Order ILIK8224 with the Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico. Steven J. Davis (ARDD) was the Laboratory Project Officer-in-Charge.

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This technical report has been reviewed and is approved for publication.

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## REPORT DOCUMENTATION PAGE

|   |  |  |                            |
|---|--|--|----------------------------|
| 1a. REPORT SECURITY CLASSIFICATION<br>Unclassified  |  | 1b. RESTRICTIVE MARKINGS   |                            |
| 2a. SECURITY CLASSIFICATION AUTHORITY   |  | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br>Approved for public release; distribution unlimited.           |                            |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE   |  |  |                            |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)   |  | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>AFWL-TR-83-132  |                            |
| 6a. NAME OF PERFORMING ORGANIZATION<br>University of New Hampshire<br>Department of Physics   | 6b. OFFICE SYMBOL<br>(If applicable)       | 7a. NAME OF MONITORING ORGANIZATION<br>Air Force Weapons Laboratory                                      |                            |
| 6c. ADDRESS (City, State and ZIP Code)<br>Durham NH 03824   |  | 7b. ADDRESS (City, State and ZIP Code)<br>Kirtland Air Force Base NM 87117                               |                            |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION   | 8b. OFFICE SYMBOL<br>(If applicable)       | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>F29601-82-K-0068                                      |                            |
| 8c. ADDRESS (City, State and ZIP Code)  |  | 10. SOURCE OF FUNDING NOS.   |                            |
|   |  | PROGRAM<br>ELEMENT NO.<br>61101F   | PROJECT<br>NO.<br>ILIR     |
|   |  | TASK<br>NO.<br>82  | WORK UNIT<br>NO.<br>24     |
| 11. TITLE (Include Security Classification) LASER SPECTROSCOPY<br>OF ALKALI ATOM-TETRAHALOETHYLENE REACTIONS  |  |  |                            |
| 12. PERSONAL AUTHOR(S)<br>Wright, John J.   |  |  |                            |
| 13a. TYPE OF REPORT<br>Final  | 13b. TIME COVERED<br>FROM 82 Jun TO 83 Dec | 14. DATE OF REPORT (Yr., Mo., Day)<br>1984, August   | 15. PAGE COUNT<br>22       |
| 16. SUPPLEMENTARY NOTATION  |  |  |                            |
| 17. COSATI CODES  |  | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)                        |                            |
| FIELD   | GROUP                                      | SUB. GR.   |                            |
|   |  | Laser, Alkali Atoms, Chemiluminescence, Spectroscopy,<br>Sulfur, Carbon, Hydrocarbons, Mass Spectroscopy |                            |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)  |  |  |                            |
| <p>The results of a series of experiments are reported to determine the origin of the chemiluminescent spectrum observed in reactions of alkali metal atoms with vapors of <math>C_2Cl_4</math> and similar halogenated <math>C_2^n</math> molecules. The emission was observed to be independent of the alkali atom and the halogen atom and, hence, attributed to a previously unobserved state of a carbon molecule, such as <math>C_2^n</math>, <math>C_3^n</math>, or <math>C_4^n</math>. Null results from laser spectroscopy suggest the emission is not to the ground state of the molecule. Initial gain measurements were also negative. These reactions are being investigated using mass spectroscopy with the aim of determining the source of the chemiluminescence and the molecular dynamics of this and related reactions.</p> <p>During the course of this research, several other chemiluminescent reactions were discovered which are also promising candidates for future investigation. The primary result from this research is that the stripping of halogen atoms from parent molecules by alkali atoms (Over)</p> |  |  |                            |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br>UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>   |  | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified   |                            |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Steven J. Davis  |  | 22b. TELEPHONE NUMBER<br>(Include Area Code)<br>(505) 844-1871   | 22c. OFFICE SYMBOL<br>ARDD |

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19. ABSTRACT (Continued)

is an exothermic process capable of producing electronically excited atoms and molecules and has apparently received little attention in the past.



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## I. INTRODUCTION

The potential for an electronic transition chemical laser from  $C_2$  Swan band chemiluminescence produced in the reactions of alkali atoms with  $CCl_4$  vapor has generated worldwide interest. Palmer and Miller (Ref. 1) first reported chemiluminescence from alkali-carbontetrahalide reactions followed by similar observations from a Russian group headed by Bugrim, et al (Ref. 2). Subsequently, Miller and Palmer (Ref. 3) and Naegeli and Palmer (Ref. 4) showed that the populations of the vibrational levels of the excited  $C_2$  state were inverted. More recently, a Chinese group, Xuechu and Nanquan (Ref. 5) and Wang et al (Ref. 6), and Luria et al (Ref. 7) have studied the relaxation kinetics of the excited  $C_2$  during the reaction. The dynamics of the reaction are still unknown except that the spectrum must result from a recombination of carbon atoms and/or molecules.

This report describes the preliminary results of similar types of reactions with alkali atoms and tetrahaloethylene molecules, such as  $C_2Cl_4$ , which produce a very different and anomalous blue-green chemiluminescence (Ref. 8).

## II. EXPERIMENTS

Figure 1 is a schematic diagram of the experimental arrangement used for most of the experiments which will be discussed in this report. The reactions took place in a 300 ml evacuated Pyrex

cell attached to a vacuum-gas handling system. The cell contained an alkali metal and was heated to maintain alkali vapor pressures in the range 1 - 100 Pa. The  $C_2Cl_4$  was admitted to the cell through a controlled leak at a rate necessary to establish a uniform luminescent glow throughout the cell. The chemiluminescent spectra were recorded with an optical multichannel analyzer.

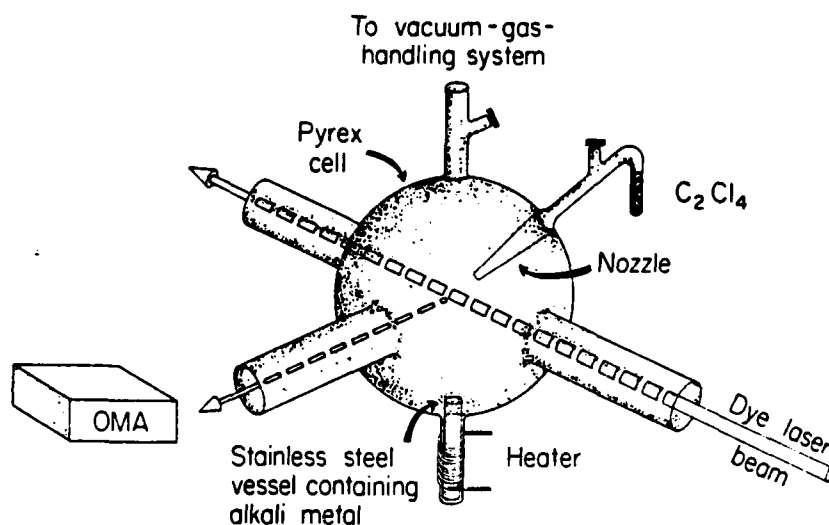


Figure 1. Experimental arrangement.

### 1. BLUE-GREEN SPECTRUM

The blue-green spectrum was observed in the following reactions:  $Li, Na, K, Rb, Cs + C_2F_4$ ,  $Na, K, Rb, Cs + C_2Cl_4$ ,  $Na, K, Rb, Cs + CF_3(CF_2)_4CF_3$  (perfluorohexane),  $Na, K, Rb, Cs + CF_3(CF_2)_4CF=CF_2$  (perfluoroheptene),  $Cs + CCl_2F-CClF_2$  (trichlorotrifluoroethane),  $K, Rb + CF_3CF_2CF_2I$  (perfluoropropyl iodide), and  $Cs + C_4F_8$ . Figure 2 shows some representative spectra. The spectra are independent of the alkali atom involved and the halogen atom.



The common element is the presence of more than one carbon molecule.

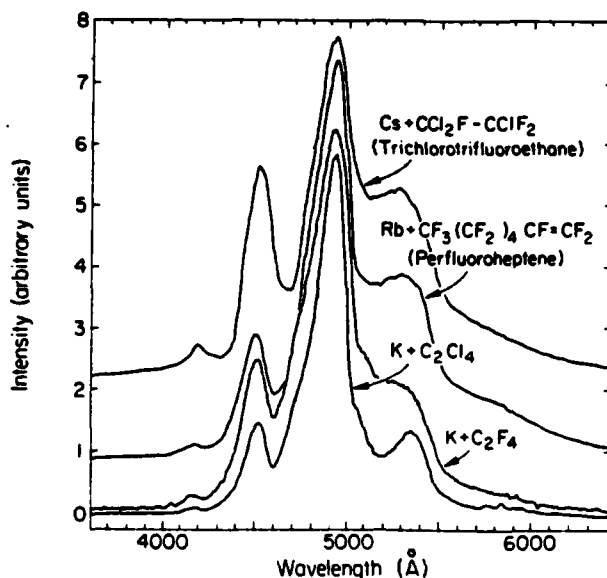


Figure 2. Representative blue-green spectra.

The spectral source has been narrowed further because it was discovered that the molecule must have carbon atoms bonded to carbon atoms, i.e. there must be either a C-C or C=C bond in the reactant molecule. The reaction with  $\text{Cl}_3\text{COCOC}\text{Cl}$  produces an inverted Swan spectrum of  $\text{C}_2$  identical to that from the reaction of  $\text{CCl}_4$  (Fig. 3). In this molecule, the carbon atoms are not bonded to each other but to a common oxygen atom.

There is also evidence that the reaction producing the blue-green spectrum requires at least one stripped  $\text{C}_2$  molecule. The reaction with trichloroethylene ( $\text{C}_2\text{HCl}_3$ ) did not produce either the blue-green spectrum or the  $\text{C}_2$  Swan spectrum. The alkali halogen bond energy is greater than the carbon-halogen bond

energy so the alkalis can strip halogens away from the carbon but the alkali-hydrogen bond energy is less than the carbon-hydrogen bond energy so in this reaction the stripping by the alkalis results in  $C_2H$  molecules.

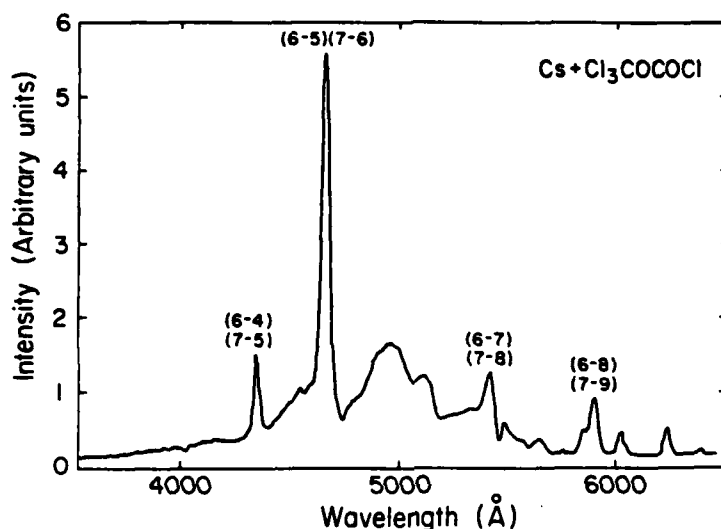


Figure 3. Population inverted  $C_2$  Swan spectrum.

In the reaction  $K + CCl_4$ , it was reported in Reference 4 that the population inversion in the Swan spectrum of  $C_2$  was independent of Argon (Ar) buffer gas pressure from 25 to 2500 Pa. Luria (Ref. 7) measured a quenching rate for the excited state of  $C_2$  due to Ar and Xueche (Ref. 5) has subsequently confirmed this (for  $Na + CCl_4$ ) and found the quenching rate to be nearly gas kinetic. The reactions of alkalis with  $CCl_4$  observed in this laboratory showed no vibrational relaxation with  $2.6 \times 10^4$  Pa of He or  $1.3 \times 10^4$  Pa of  $N_2$  buffer gas. Similar results with  $C_2Cl_4$  and

the blue-green spectrum. Figure 4 shows the results of adding 25 torr (3325 Pa) of He to a Cs + C<sub>2</sub>Cl<sub>4</sub> reaction cell. The blue-green spectrum is unaltered. The addition of two atmospheres of He did not alter the spectrum other than to reduce the intensity due to the reduced diffusion rate.

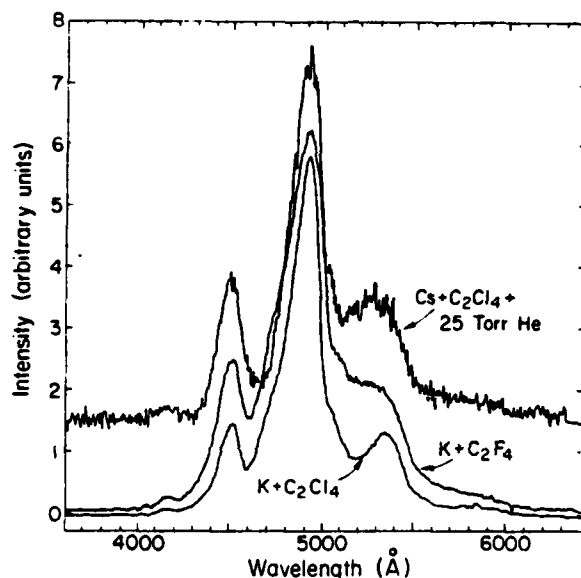


Figure 4. Effect of buffer gas on the blue-green spectrum.

In its high resolution mode, the OMA has a resolution of 1.4 angstroms per channel. With this resolution, the blue-green spectrum still appears structureless.

## 2. LASER SPECTROSCOPY

Numerous laser spectroscopy experiments using continuous wave and pulsed dye lasers and an Ar<sup>+</sup> laser failed to produce any detectable laser induced emission from reaction cells. The Ar<sup>+</sup>

laser has several lines which overlap the observed blue-green emission. No laser induced fluorescence was detected during the reaction due to absorption of  $\text{Ar}^+$  laser light. In an attempt to monitor the observed blue-green emission as a function of  $\text{C}_2$  density (and to determine if  $\text{C}_2$  was present) the cw dye laser was tuned to the 1-0 transition (5635 Å) of the  $\text{C}_2$  Swan system and the  $\text{N}_2$ -pumped dye laser was tuned to the 0-0 transition (5165 Å) of the same system and passed through reaction cells burning Cs and K +  $\text{C}_2\text{Cl}_4$  and perfluorohexane. No  $\text{C}_2$  emission was ever observed. However, this is not conclusive evidence that  $\text{C}_2$  is not present since laser induced emission was not detected in a DC discharge in  $\text{C}_2\text{Cl}_4$  which produced  $\text{C}_2$  Swan band emission. The lower state of the Swan system is not the ground X state of  $\text{C}_2$  but lies about  $700\text{ cm}^{-1}$  above it. The near infrared X - A transitions of  $\text{C}_2$  could not be directly excited but A - X emission was never observed from either the alkali- $\text{CCl}_4$  or alkali- $\text{C}_2\text{Cl}_4$  reactions.

### 3. GAIN MEASUREMENTS

Several attempts were made to detect gain from the blue-green emission using the 4880  $\text{Ar}^+$  laser line and a multiple-pass reaction cell as shown schematically in Figure 5. Each laser pass went through about 10 cm of the reaction volume. The following configurations were attempted: 9 passes through Rb + perfluoroheptene, 9 passes through Cs + perfluorohexane, 7 passes through K + perfluorohexane and 5 passes through the same reaction with the laser beam expanded to fill the volume, and Cs +

perfluorohexane with a buffer gas added. The results were all negative. Future gain measurements are planned monitoring the decay time of the  $N_2$ -pumped dye laser pulse and a reaction cell inside an etalon cavity. This arrangement will circumvent the problems encountered in these experiments with laser beam jitter and refraction effects.

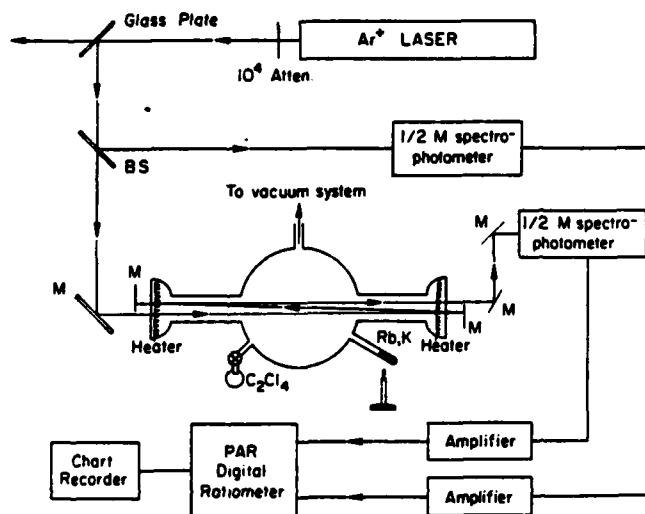


Figure 5. Gain measurement apparatus.

#### 4. MASS SPECTROSCOPY

Since laser spectroscopy was unable to shed any light on the origin of the blue-green emission, it was decided to try mass spectroscopy. The aim was, and still is, to monitor the reaction products as a function of the reactant densities and blue-green emission to determine the source of the emission and the reaction

dynamics. The Air Force Weapons Laboratory loaned a mass spectrometer for this purpose. It was determined that the reaction could be run into the spectrometer and that reaction products could be detected during and after the reaction. The cracking by the mass spectrometer makes it difficult to distinguish reaction products from mass spectrometer cracking products. Several runs were made with inconsistent results before it was realized that reactions with the alkali metal on the cell walls was the dominate effect that was observed with the mass spectrometer. A new cell configuration was designed, but before it could be tested, the mass spectrometer self-destructed. Subsequently, a quadrupole gas analyzer was purchased and the work is continuing.

## 5. OTHER RELATED EXPERIMENTS

During the course of these experiments several other interesting effects were observed which will be investigated further. To summarize the basic findings, the gas phase reaction of alkali metal atoms with halogenated molecules is exothermic and produces excited states in a variety of atoms and molecules.

a.  $C_3$  Spectrum Figure 6 shows the spectrum obtained from the reaction of Cs and  $C_3F_7I$  (perfluoropropyl iodide). In addition to the usual blue-green spectrum and some atomic Cs lines, there is the Comet Tail spectrum of  $C_3$  which peaks around 4050 Å. To our knowledge, this is the first observation of a chemically produced  $C_3$  spectrum.

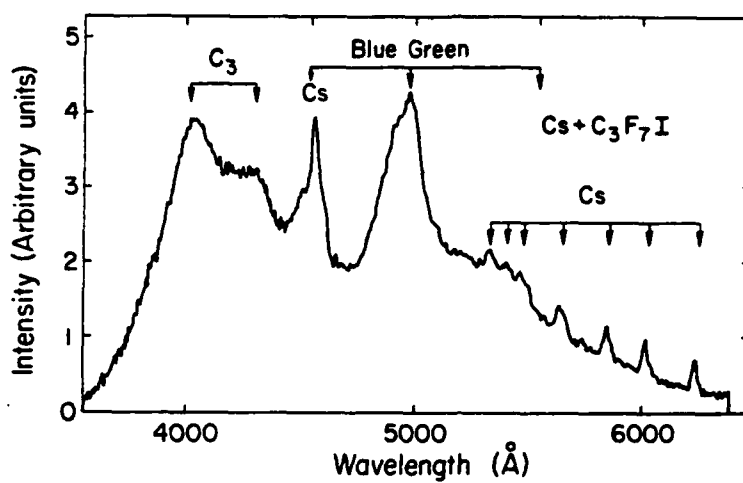


Figure 6. Chemically produced  $C_3$  spectrum.

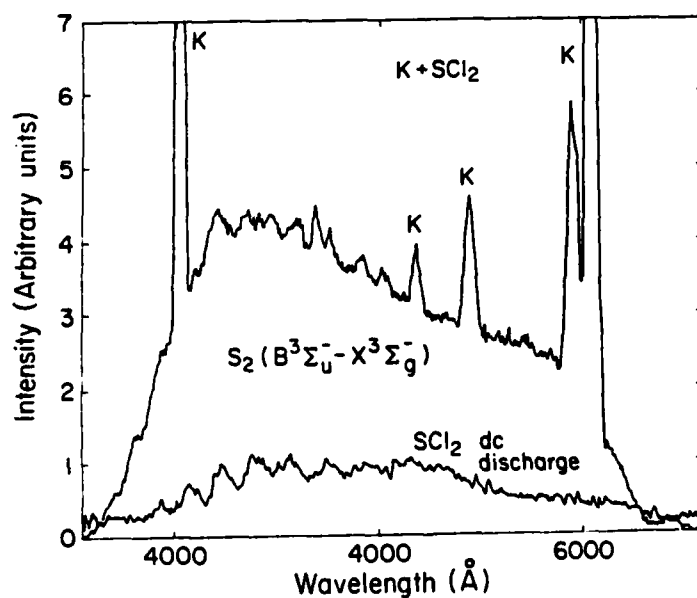


Figure 7. Chemically produced  $S_2$  spectrum.

b.  $S_2$  Spectrum Figure 7 shows a typical spectrum from the reaction of K and  $SCl_2$ . Analogous to the reaction with  $CCl_4$  producing the  $C_2$  recombination Swan spectrum, the reaction with  $SCl_2$  produces electronically excited  $S_2$ . The emission has been identified as that from the B - X system, which is a known lasing system.

c. Atomic Cs Spectrum The reaction of Cs atoms with  $SCl_2$  does not produce the recombination spectrum of  $S_2$  shown in Figure 7 but produces a bright flame which consists almost entirely of atomic Cs lines. Figure 8 shows part of the spectrum. The transitions identified originate from the s and d states of the  $n=7, 8, 9, 10, 11$ , and 12 levels and terminate at the 6p state. There are several infrared transitions which are allowed but which are outside the range of the detector. These high lying Rydberg states have progressively longer lifetimes and it is possible that population inversions exist between some of these upper levels.

d.  $K_2$  Spectrum In the process of trying to understand the dynamics of the  $C_2$  Swan system production, an attempt was made to alter the vibrational populations with inert buffer gases. As stated earlier, there was no buffer gas effect with the  $K + CCl_4$  reaction. However, Figure 9 shows that the addition of a buffer gas to the reaction of  $K + CBr_4$  produced a more thermal vibrational distribution in the Swan spectrum of  $C_2$ . (This new information was considered to be relatively useless since it could not be determined whether the effect of the buffer gas occurred before or after the formation of  $C_2$  molecules.) Figure



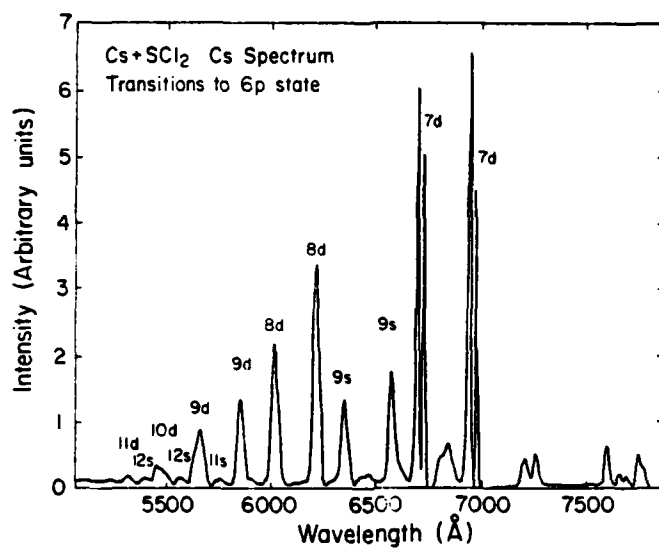


Figure 8. Chemically produced Cs Rydberg series.

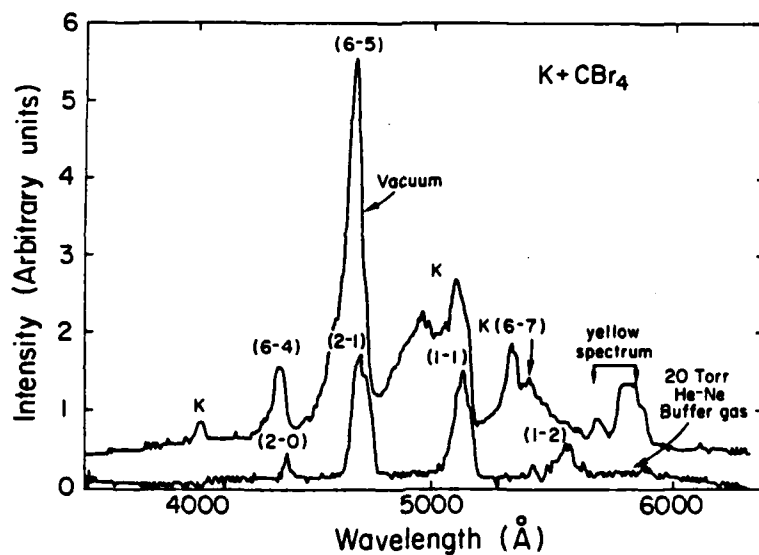


Figure 9. Vibrational relaxation of the C<sub>2</sub> Swan system.

9 also shows a yellow emission in the range 5700-5850Å. Under the proper conditions, this spectrum dominated the flame, at which time the entire cell glowed yellow and the OMA showed no other spectral components. The effect was reproducible. Figure 10 shows this yellow spectrum under higher resolution. It has not been identified but the most likely candidate, on the basis of elimination, is  $K_2$ . The  $Rb + CBr_4$  reaction showed no such spectrum and neither did the reaction of  $K + Br_2$  or  $Cl_4$ . This effect will be investigated further.

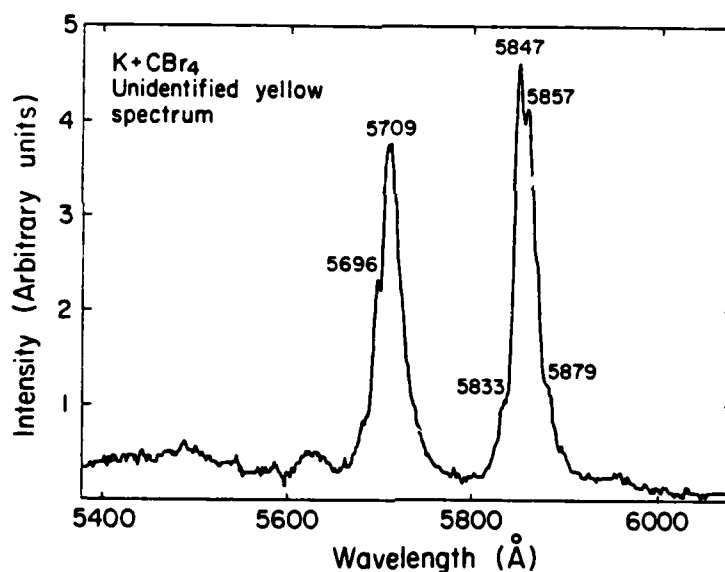


Figure 10. Unidentified yellow spectrum from  $K + CBr_4$ .

### III. CONCLUSIONS

An extensive amount of spectroscopic information has been accumulated on the chemiluminescent reactions of alkali atoms

with halogenated hydrocarbons but as yet the source of the anomalous blue-green luminescence has not been identified. The observation of this anomalous emission was reported in a previously published paper (Ref. 8) and it was speculated that the source might be  $C_4$  molecules. This was based on theoretical calculations of the  $C_4$  spectrum and an analogy between  $CCl_4$  producing  $C_2$  emission and  $C_2Cl_4$  producing  $C_4$  emission. This explanation cannot be ruled out. Other possibilities include previously unobserved  $C_2$  emission from high lying levels of the A state (i.e. A - X emission) or highly perturbed Swan emission. Apparently, little is known about the structure of the A state for  $v'$  greater than 8 because these levels are not easily accessible from the lower levels of the X state and recombination (observed in discharges) favors formation of the triplet system, i.e., Swan band emission. If it is dimer emission, it is difficult to account for the broad, unstructured emission width and why  $C_2$  Swan emission is not observed. Another possibility is emission from an intermediate process. In  $C_2Cl_4$  the carbon atoms share a double bond. In  $C_2Cl_2$  the carbon atoms share a triple bond. The difference in bond energies is about 58 kcal/mole or 5000 Å. It may be possible that when an alkali strips a Cl atom from double bonded  $C_2Cl_3$  to produce triple bonded  $C_2Cl_2$  the energy is given up radiatively. This might be independent of the alkali and halogen and account for the broad emission width. The four emission peaks may reflect the order in which the halogen atoms are stripped. Yet another possibility is previously unobserved emission from  $C_3$  molecules. It is hoped that the new

mass spectrometer will provide the additional information necessary to determine the source of this emission.

Since there is considerable interest in the dynamics of the alkali- $\text{CCl}_4$  reaction, it is hoped that the use of the mass spectrometer will shed light on this system as well. The analysis in this case is simplified because the emission is known to originate from  $\text{C}_2$  molecules.

The main conclusion drawn from this research is that the reactions of alkali atoms with halogenated molecules produce excited states of molecules and atoms, several of which are previously unobserved. Continued research on the molecular dynamics involved in these reactions should enhance the basic knowledge and aid the search for an electronic transition chemical laser.

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